

CHARACTERIZATION OF SYNTHETIC LIQUID FUELS

by

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INTRODUCTION

In order to decide what is the best use of a fuel, natural or synthetic, and/or which one out of a number of fuels is the best for a specific application, it is necessary to (1) know the characteristics of each fuel, and (2) be able to compare the characteristics of one fuel directly with those of another.

Experience has shown that in order to obtain meaningful results in analyzing petroleum crudes and residues, it is necessary to separate a sample into a certain number of well-defined fractions and to analyze these fractions in detail. Conclusions as to the composition of the original sample are then arrived at by combining the results of the analyses on each fraction in a manner consistent with the steps performed to obtain them. This same approach is used for the synthetic liquid fuels and this paper reports our results obtained on such materials.

The literature on tar sands and tar sand bitumen is not very rich, as compared to that on shale oils and coal. Most of the currently available data are limited to the material of the Athabasca deposit, in the Province of Alberta, Canada, primarily because of its size and location. Detailed general information on the Athabasca tar sands and tar sand bitumen is available in References 1 and 2. In addition, the analysis of this bitumen has been reported by various workers.³⁻⁷

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The literature on oil shale and shale oils is much richer and goes back several decades. However, due to its size and location, most of the literature deals only with one oil shale formation, the Green River Formation.

Space limitations prohibit a literature survey here; however, much information on oil shales and shale oils, in general, is found in References 8 through 11, while the remainder of the available data can be divided into two general categories.

1. Data obtained on shale oils produced by various retorting methods with the purpose of obtaining a fuel.¹²⁻²³
2. Data obtained on shale oils produced by solvent extraction methods for geological and geochemical studies.²⁴⁻³⁵

An enormous amount of data dealing with all aspects of the chemical and physical properties of coal is available; however, only four reviews have been referenced which are particularly comprehensive.³⁶⁻³⁹

EXPERIMENTAL

A. Samples Preparation

The coal liquids were derived from the catalytic liquefaction of Pittsburgh Seam bituminous and Wyoming subbituminous coals. The analysis of these coals is given in Table I. The coals were liquefied in a bench-scale catalytic unit using cyclone overhead product as recycle solvent to insure that the liquid products were derived from the coal and not the solvent. The product streams from the unit consisted of gases, water, light ends typically boiling in the range of 150-500°F, and slurry. The slurry product was filtered to remove the undissolved coal plus mineral matter prior to analysis. Based on

a calculated material balance for processing 1.0 ton of as-received Pittsburgh Seam coal, the light ends and filtrate yields were 135 and 1,350 pounds, respectively. Similarly, yields of light ends and filtrate from the subbituminous coal were 265 and 740 pounds, respectively. The term "coal liquids" as used hereafter refers to the filtered slurry product with a boiling point above 130°F.

A sample of raw bitumen recovered from Athabasca tar sands was analyzed without further upgrading. This sample was provided by Sun Oil Company.

Three distillate cuts of shale oil were obtained from The Oil Shale Corporation and were also analyzed without further upgrading.

B. Separation Into Fractions

The separation procedure, developed for petroleum crudes and residues,⁴⁰ is illustrated in Figure 1. This procedure is applicable to samples having a boiling point higher than 470°F.

The distillation step is necessary only with samples containing low boiling materials. These materials must be removed since they would be lost during the subsequent steps in which solvents are used and then evaporated to recover the fractions.

The material boiling above 470°F is separated into oils, resins, and n-pentane insoluble residue. The residue is separated into asphaltenes and benzene insolubles by extraction with benzene while the oils are separated into aromatics and saturates. The saturates can be further separated into n-paraffins and non-n-paraffins with 5 Å molecular sieves,⁴¹ while the aromatics are separated into three additional fractions on alumina.⁴² The results of the separations are listed in Table II.

C. Method of Analyses

Unless otherwise specified, the average molecular weights were obtained by vapor pressure osmometry (VPO) in benzene according to ASTM D2503. For the aromatic fractions, an average molecular weight is also obtained by ^1H NMR and reported in the respective tables.

Carbon and hydrogen were determined by a microcombustion method; nitrogen by a micro Kjeldahl method; oxygen by neutron activation or by a modified Unterzaucher method; and sulfur by a combustion method similar to ASTM D1552. Tables III and IV report all the molecular weight and elemental data.

The simulated distillation data (Table V) and the FIA analyses of the distillates (Table II) were obtained by techniques similar to those described by Mayer, et al.⁴³

The mass spectrometric analyses of the saturates fractions (Table VI) were obtained by an in-house method similar to that of Hood and O'Neal.⁴⁴

The aromatic fractions were analyzed by the proton NMR method of Clutter, et al.⁴⁵ and the results are reported in Tables VII and VIII.

DISCUSSION OF RESULTS

A. Tar Sand Bitumen

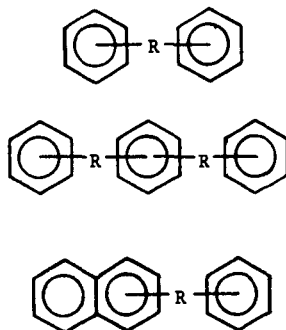
This material is very viscous, black, and contains a considerable amount of sulfur, some nitrogen and oxygen, and no light ends (see Tables II and III). The saturate fraction amounts to about 17% and is a clear colorless liquid with an average molecular weight of 365 (Table III). The carbon number ranges from about 14 to well above 44 (Figure 2) and its final boiling point is above 1,000°F (Table V). These characteristics are reconciled

by the observation that no alkanes are present as shown by: (1) the mass spectrometric data (Table VI); (2) the fact that no material was removed when this fraction was treated with 5 Å molecular sieves; and, (3) the lack of sharp peaks on the GLC of this fraction (Figure 2). In addition the inability to remove alkanes from this type of material was also reported by Speight.⁴ The condensed and noncondensed cycloalkanes are evenly distributed, and more than half of the condensed cycloalkanes have only two rings, as indicated by mass spectrometry (Table VI).

The aromatic fraction accounts for almost half of the bitumen with the largest contribution made by the di- + triaromatics (Table II). The aromatic fractions were further characterized by a ¹H NMR spectroscopic technique. This method, developed for petroleum crudes and fractions, calculates from the NMR spectrum a set of average parameters used to describe an "average molecule". In this method, three assumptions are necessary which place constraints on its applicability. The assumptions are: (1) no aromatic fused ring systems larger than three are present; (2) the resonances of the unsubstituted non-bridge aromatic ring carbon protons are sufficiently separated in the proton NMR spectrum so that the ratio of mono- to di- to triaromatics can be determined; and, (3) the number of substituent groups, on the average, is the same for mono-, di-, and triaromatics. The last two assumptions are probably as valid for synthetic liquid fuels as for petroleum. The first assumption is partially satisfied by the separation steps which provide three fractions two of which (the monoaromatics and the di + triaromatics) are free of fused ring systems larger than three rings. The proton NMR analysis of the third fraction (the polyaromatics), which does contain four or more rings, condensed and noncondensed, is then only qualitative.

Figure 3 shows the spectra of the three aromatic subfractions and Table VII the results of the calculations. The monoaromatic subfraction is shown by NMR to be free from other aromatic types and to have many short alkyl substituents and at least one naphthene ring per molecule. The average molecular weight obtained by NMR agrees very well with that determined by VPO.

The di- + triaromatic subfraction analyzes as 54% "monoaromatics" and 47% "diaromatics" by proton NMR. The average molecule also contains many short alkyl substituents, more than one aromatic ring and one naphthene ring. The average molecular weight calculated from NMR is lower than that obtained by VPO. These data indicate that noncondensed di- and triaromatics are present in this subfraction. Compounds such as



are di- and triaromatics and are all separated as such by the alumina column. Proton NMR, however, will see the first two as monoaromatics and the last one as a monoaromatic and a diaromatic, and all the calculations are affected

accordingly. There is no way to circumvent this problem until the condensed and noncondensed aromatics can be separated from each other. It must be pointed out, however, that the presence of noncondensed systems could not have been detected by separation or spectroscopic techniques alone. Both must be used and one must support the other.

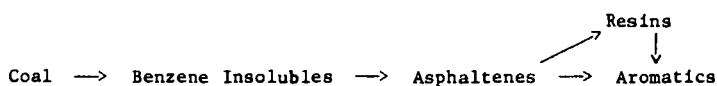
The molecular weight of the polyaromatic fraction as calculated by NMR is well below that determined by VPO. As pointed out earlier the NMR analysis of this fraction can only be semiquantitative because tetra- and higher aromatic systems will be calculated as mono- and diaromatics and all the calculations will be affected accordingly. In our separation scheme all of the polar non-hydrocarbons are concentrated in the resin fractions. Only ethers and thioethers are included in the oil and are eventually concentrated in the di + triaromatics and polyaromatics, as the data in Table III show. Also only half of the saturates are condensed cycloalkanes, mainly of two and three rings. These observations are indirect evidence that no significant amounts of large condensed systems are present, and that at least part of the polyaromatic fraction consists of noncondensed mono-, di-, and triaromatic units.

The resins and asphaltenes have not been analyzed beyond the extent shown by the tables. The resins can be fractionated and analyzed in more detail using methods developed for petroleum resins by Jewell⁴⁶ and McKay⁴⁷. This analysis, however, is beyond the scope of this work.

B. Coal Liquids

The two coal liquids contain about the same amount of material boiling below 470°F very little saturates, and substantial amounts of aromatics, mainly di- + triaromatics (Table II). The liquids from the Big Horn coal, however, contain more aromatics and less resins, asphaltenes,

and benzene insolubles than the liquids from Pittsburgh Seam coal. This is not surprising considering the fact that higher rank coals are harder to hydrogenate and that the liquefaction process is believed to follow the path:



The distillates were fractionated into saturates, aromatics, and olefins by FIA as already mentioned. Attempts to further characterize the FIA fractions by GLC were not successful.

By GLC methods, it is possible to obtain detailed quantitative analyses of saturates up to C_9 , of mono-olefins up to C_7 , and of aromatics up to C_{10} .⁴³ The liquid chromatographic steps cannot handle materials boiling below $n-C_{12}$. Therefore, there is a gap in the analysis of the distillate fractions on which a detailed analysis cannot be readily, routinely and inexpensively obtained. This gap includes all the C_8 to C_{12} saturates, all the C_{11} - C_{12} aromatics, and all the heterocompounds and olefins that are present in this fraction.

The saturates boiling above $470^\circ F$ were analyzed by mass spectrometry and appear to contain alkanes but predominantly cycloparaffins. The alkanes appearing in these liquids may not be part of the coal network, but may simply be embedded in it. The primary coal structure is generally believed to be formed of small aromatic units held together by short links, mainly methylene, ethylene, propylene, and ethers.⁴⁸⁻⁵⁵ However, the alkanes present in these fractions have a carbon range between 12 and 30, as shown

by the chromatogram in Figure 4, and should not be the result of the decomposition of coal. Vahrman, et al., have shown that small molecules can be extracted from coal by non-destructive methods.⁵⁶⁻⁶¹

The cyclic saturates can also be entrained in the coal pores, but they can also be the result of the hydrogenation and liquefaction process. In order to establish the actual origin of these saturates, it would be necessary to carry out a considerable amount of work which would be valuable but is beyond the present scope.

The aromatic fractions were also examined by ^1H NMR and examples of spectra are shown in Figure 5. The liquids are derived from coals of different ranks and this is reflected in the size of each fraction as already pointed out. However, at least for these materials, the characteristics of corresponding fractions are very similar regardless of their origin. This is evident from the mass spectrometric analysis of the saturates and is further shown by the analysis of the aromatic fractions. The NMR spectra of corresponding fractions from the two coal liquids are almost superimposable, and for this reason only one set of spectra is shown here, that for the Big Horn coal liquids. The similarity of the aromatics from the two coals is made quite clear by the NMR data shown in Table VII.

The two monoaromatic and di- + triaromatic fractions are practically indistinguishable from each other except for a slightly higher molecular weight of the fractions from the Pitt Seam coal liquids. The spectra of the polyaromatic fractions were too weak and unresolved, and no meaningful calculations could be made from them. Similar problems were encountered when it was attempted to analyze the asphaltenes by NMR; methods have to be developed in order to analyze polyaromatic and asphaltene fractions.

C. Shale Oils

As indicated by the data in Table II, only Cut I of the shale oils contains a considerable amount of material boiling below 470°F, as would be expected from the low boiling range of this fraction (Table V). This distillate was fractionated into saturates, aromatics, and olefins by preparative FIA techniques, but a GLC analysis of these fractions proved unfruitful for the same problems mentioned above in the case of the coal liquids.

A large portion of the remainder of the shale oil consists of resins with smaller contributions from the saturates and aromatics. The amount of asphaltenes is really insignificant, and a larger contribution would actually be surprising since these are retorting products.

The shale oils are rich in olefins; in our separation scheme free olefins are concentrated in the saturate fractions. The IR spectra of all three saturate fractions show the characteristic olefin bands at 6.1, 10.1, 10.35, and 11.0 microns. However, no attempt has been made to characterize these olefins in detail, mainly because they are easily hydrogenated.

The mass spectrometric analyses of the saturate fractions are reported in Table VI. These fractions appear to be composed mostly of alkanes and noncondensed cycloalkanes with smaller amounts of condensed cycloalkanes, mainly two- and three-ring systems. However, due to the presence of olefins in these fractions the analyses are only semiquantitative. In fact, an olefin should make a contribution to the cycloalkane group type which has the same molecular weight. That is, a mono-olefin will contribute to the cycloalkanes, a diolefin or a cyclic olefin will contribute to the bicycloalkanes, etc. However, the extent of these contributions has never been determined.

No carbon number predominance was detected in the saturate fraction from Cut I and Cut II. The chromatogram of the saturates from Cut III is shown in Figure 6 and an odd-over-even carbon number predominance is evident for the higher carbon number region.

The aromatic subfractions have also been analyzed by proton NMR, and Figure 7 shows the spectra obtained with the fractions from Cut II, and the results of the calculations for all of the fractions are shown in Table VIII. The monoaromatics are free of other aromatic types, have a very low aromaticity, are highly substituted, and at least two of the substituents are naphthene rings. Anders, et al.,³⁴ and Gallegos³⁵ have isolated and identified a large number of alkylbenzenes, alkyltetralines, dinaphthenebenzenes, and trinaphthenebenzenes from Green River shale oils.

The di- + triaromatics contain large amounts of non-condensed systems and a much higher aromaticity due to a decrease in the number and size of the substituents. The apparent decrease in the average molecular weights (calculated) is due in part to the presence of the noncondensed systems. As pointed out earlier, one molecule of 1,4-diphenylbutane, for example, will be detected by ^1H NMR as 2 molecules of ethylbenzenes, and the calculation will be affected accordingly. An apparent decrease in the average molecular weight is then seen and this decrease will be even more marked if the concentration of noncondensed triaromatics is significant. Anders and Robinson²⁸ have reported the evidence of large amounts of perhydrocarotenes, and Gallegos³⁵ has isolated and identified various phenyl (cyclohexyl) alkanes. By complete dehydrogenation of these materials, during maturation, noncondensed systems would be formed.

The ^1H NMR analyses of the polyaromatic fractions present the same problems already mentioned in the discussion of the corresponding fractions from the other synthetics. While noncondensed systems are certainly present, no conclusion can be drawn from these data as to the true composition of these fractions.

D. Comparison of Fuels

The separation data of Table II show immediately some gross differences and similarities among the various fuels analyzed. Both coal liquids have a considerable amount of low boiling material which is made up of saturates and aromatics in about equal concentration. Similarly, the shale oil contains low boiling material, while the tar sand bitumen does not.

Of the material boiling above 470°F , the tar sand bitumen contains more saturates than the other fuels. As pointed out above, these saturates are unique in that they do not contain free alkanes, while the saturates from the other fuels contain from 22 to 40% alkanes as determined by mass spectrometry (Table VI).

Only the Big Horn coal liquids have more condensed cycloalkanes than noncondensed cycloalkanes. The tar sands have an equal distribution of the two types of saturates, and the remaining fuels have a higher concentration of noncondensed cycloalkanes; the effect of the olefins on the mass analysis of the saturates from the shale oils must, however, be kept in mind in making this comparison.

The fact that only the coal liquids show condensed systems with up to six rings, and that the Pitt Seam coal liquids (products from a higher rank coal) have a higher concentration of these condensed systems is also worth pointing out. However, the amount of the total saturates in the coal liquids is insignificant from a production and refining point of view.

The aromatic content of the fuels ranges from about 15% to 58%, and in every case the largest contribution is made by the di- + triaromatics. In addition to the differences in the quantity of the aromatic fractions, as shown by the data in Table II, the characteristics of each fraction vary depending on its origin. The variations are shown pictorially by the NMR spectra, and more tangibly by the NMR data listed in Tables VII and VIII. The tar sand bitumen fractions have, in general, a lower aromaticity than the shale oil and coal liquid fractions. This is due to a higher number and a larger size of the substituents. The coal liquids have the highest concentration of condensed di- + triaromatics, and the tar sand bitumen the lowest. Conversely, the amount of noncondensed systems is highest in the tar sand bitumen and lowest in the coal liquids.

Perhaps, where these fuels differ most is in the amount of resins, asphaltenes, and benzene insolubles. The shale oils contain a very large amount of resins from 12 to 69%, or approximately 50% by weight on a total shale oil basis. The tar sand bitumen contains only half as much resins and the coal liquids contain much less. On the other hand, the asphaltenes are significant in the tar sand bitumen and in the Pitt Seam coal liquids. These latter materials are the only ones to contain a significant amount of benzene insolubles.

CONCLUSION

Coal liquids and other synthetic liquid fuels can be analyzed by a modification of the methods normally used for petroleum crudes and products. These methods of analysis are relatively fast, require only a few grams of

sample, provide discrete fractions which can be characterized in as much detail as desired with available techniques, and provide comparative compositional profiles for fuels from various sources, natural and synthetic. The methods have limitations, as indicated throughout the paper. However, as new procedures are developed to take care of these limitations, they can readily be incorporated.

RGR;qrc/mag

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TABLE I
ANALYSIS OF COAL SAMPLES

Coal Sources	Pittsburgh Seam	Big Horn, Wyoming
Rank	Bituminous	Subbituminous
Proximate Analysis(wt. %)		
Moisture	2.5	19.6
Volatile Matter	33.4	34.0
Fixed Carbon	57.4	41.2
Ash	6.7	5.2
Chemical Analysis(wt. %) (Moisture Free Basis)		
Carbon	78.68	69.15
Hydrogen	4.96	4.69
Nitrogen	1.57	1.23
Oxygen (Difference)	6.29	17.75
Sulfur	1.65	0.72
Ash	6.87	6.46

TABLE II

SEPARATION DATA (Weight Percent)									
Sample Description	Tar Sands		Coal Liquids			Shale Oils			
	Bitumen	Big Horn	Coal	Pitt Seam	Coal	Cut I	Cut II	Cut III	
Boiling Range, °F	600+	130+	130+	130+	100.0	140-540	540-680	660+	
Fraction of Total Sample	100.0	100.0	100.0	100.0	100.0	32.6	10.4	57.0	
Distillate (B.P. <470°F)	0.0	28.3	25.2	25.2	66.5	2.7	0.0		
Saturates*	0.0	14.0	14.2	14.3	14.3	-	0.0		
Aromatics*	0.0	14.2	10.8	33.9	33.9	-	0.0		
Olefins*	0.0	0.1	0.2	18.3	18.3	-	0.0		
Residue (B.P. >470°F)	100.0	71.7	74.8	33.5	97.3	100.0			
Saturates	16.5	3.6	1.8	6.0	31.0	12.3			
Aromatics	47.8	58.3	36.2	14.7	27.0	15.8			
Monoaromatics	7.0	9.0	5.9	8.3	8.0	5.3			
Di- + Triaromatics	30.1	42.0	26.7	4.2	13.4	9.3			
Polyaromatics	10.7	7.3	3.6	2.3	5.6	1.3			
Resins (Non-hydrocarbons)	25.9	8.3	11.1	12.1	38.6	68.6			
Asphaltenes	9.8	1.5	20.3	0.7	0.8	3.3			
Benzene Insolubles	<0.1	<0.1	5.5	<0.1	<0.1	<0.1			

* By FIA, ASTM D 1319.

TABLE III

CHEMICAL ANALYSIS AND MOLECULAR WEIGHTS OF TAR
SANDS BITUMEN, COAL LIQUIDS, AND THEIR FRACTIONS

	<u>Mol.</u> <u>Wt.</u>	<u>C</u> <u>Wt. %</u>	<u>H</u> <u>Wt. %</u>	<u>N</u> <u>Wt. %</u>	<u>O</u> <u>Wt. %</u>	<u>S</u> <u>Wt. %</u>
<u>Tar Sands Bitumen</u>	-	82.98	10.42	0.42	1.15	4.60
Saturates	365	86.00	14.00	--	--	--
Aromatics	460	--	--	--	--	--
Monoaromatics	360	88.55	11.36	--	--	--
Di- +Triaromatics	365	85.04	9.45	0.02	1.14	3.80
Polyaromatics	1,400	79.36	9.57	0.42	3.40	6.89
Resins	1,300	81.15	9.04	1.34	3.35	5.31
Asphaltenes	5,100	78.84	7.80	1.19	4.53	8.46
 <u>Big Horn Coal Liquids</u>	 -	 89.18	 8.97	 0.40	 1.03	 0.04
Saturates	300	86.12	13.65	--	--	--
Aromatics	222					
Monoaromatics	285	88.09	10.10	0.06	1.82	0.00
Di- +Triaromatics	220	92.38	7.13	0.01	0.80	0.15
Polyaromatics	-	84.19	6.60	0.20	7.80	0.97
Resins	380	83.84	7.09	1.62	7.15	0.30
Asphaltenes	-	87.37	6.06	1.25	4.92	0.62
Benzene Insolubles	-	--	--	--	--	--
 <u>Pitt Seam Coal Liquids</u>	 -	 89.05	 8.18	 0.82	 1.47	 0.17
Saturates	-	85.40	14.17	--	--	--
Aromatics	240	--	--	--	--	--
Monoaromatics	290	--	--	--	--	--
Di- +Triaromatics	235	92.52	7.20	0.01	0.67	0.35
Polyaromatics		--	--	0.05	7.75	0.34
Resins	440	81.30	7.33	1.37	5.77	0.42
Asphaltenes	775	87.73	6.86	1.76	3.92	0.38
Benzene Insolubles	-	85.87	5.46	2.12	5.64	0.57

TABLE IV

CHEMICAL ANALYSIS AND MOLECULAR WEIGHTS OF
SHALE OIL FRACTIONS

	Mol. Wt.	C Wt. %	H Wt. %	N Wt. %	O Wt. %	S Wt. %
<u>Cut I, Total</u>	145 ^a	85.30	12.12	0.98	0.98	0.80
Distillate	130 ^a	85.99	12.50	0.63	0.99	0.75
Saturates	230 ^a	85.84	14.31	--	--	--
Aromatics	170 ^b	85.44	10.09	0.25	2.17	2.05
Monoaromatics	240 ^b	83.26	11.65	<0.01	4.80	<0.01
Di- +Triaromatics	190 ^b	86.35	8.27	0.02	5.06	<0.01
Polyaromatics	200 ^b	76.89	9.76	0.35	10.52	2.46
Resins	445	75.89	8.38	1.28	10.82	3.44
 <u>Cut II, Total</u>	 260	 84.68	 11.07	 2.10	 1.23	 0.68
Saturates	266 ^a	85.99	14.34	--	--	--
Aromatics	325	--	--	--	--	--
Monoaromatics	390	86.61	12.07	<0.01	1.67	<0.01
Di- +Triaromatics	290	87.79	9.26	<0.01	1.70	1.84
Polyaromatics	-	78.97	9.58	0.71	9.12	0.39
Resins	420	78.44	8.66	2.63	7.36	2.04
Asphaltenes	-	--	--	--	--	--
 <u>Cut III, Total</u>	 420	 84.65	 10.17	 2.97	 1.68	 0.78
Saturates	390	85.61	14.25	--	--	--
Aromatics	-	84.35	10.40	<0.01	4.44	0.90
Monoaromatics	-	84.14	11.85	<0.01	4.49	<0.01
Di- +Triaromatics	370	86.23	9.54	0.08	1.75	1.73
Polyaromatics	-	--	--	0.84	6.25	0.50
Resins	950	79.95	8.56	2.50	3.58	0.93
Asphaltenes	c	83.12	7.45	4.63	4.23	0.49

^aFrom GLC data.^bFrom low voltage mass data.^cWill not dissolve in benzene.

TABLE V
SIMULATED
DISTILLATION DATA

IBP, °F 1% off at 5 10 20 30 40 50 60 70 80 90 95 99 FBP	Tar Sand Bitumen Saturates	COAL LIQUIDS				SHALE OILS					
		Big Horn		Pitt Seam		Distil-		late			
		Total		Total		From		Saturates			
		Distillates	Heavy Saturates	Distillates	Heavy Saturates	Cut I	Cut II	Cut I	Cut II	Cut III	
	402	136	460	132	440	118	433	481	491		
	460	170	480	170	457	146	443	517	545		
	504	197	520	195	501	174	463	562	621		
	557	223	539	215	532	204	480	576	659		
	601	273	569	247	563	235	498	600	697		
	629	326	598	289	592	261	515	613	749		
	670	367	622	335	633	289	531	624	779		
	706	394	647	371	667	312	545	630	806		
	743	420	690	404	710	342	557	641	824		
	786	450	728	431	760	361	565	657	848		
	828	483	769	470	798	391	572	682	879		
	870	532	814	520	858	435	585	703	918		
	891	564	849	551	897	465	594	736	956		
	940	623	894	602	984	516	615	797	1,014		
	954*	696	917*	664	1,016*	563	634	831	1,094		

* GLC trace does not return to base line indicating material boiling higher than 1,000°F.

Table VI
MASS SPECTROMETRIC ANALYSIS OF SATURATES
(Volume Percent)

Weight % of Frac. in Sample	Tar Sand Bitumen	COAL LIQUIDS			SHALE OILS		
		Big Horn Coal	Pitt Seam Coal		Cut I	Cut II	Cut III
	16.5	3.6	1.8		6.0	31.0	12.3
Alkanes	0.0	39.9	22.0		42.2	34.4	29.4
Noncondensed Cycloalkanes	48.0	23.8	43.9		40.8	47.1	46.2
Condensed Cycloalkanes	47.9	32.2	30.4		15.4	16.6	22.5
2 Rings	26.7	16.3	16.2		11.3	11.8	8.9
3 Rings	14.0	9.5	7.2		3.8	4.0	11.1
4 Rings	6.5	4.1	4.2		0.3	0.9	2.5
5 Rings	0.7	1.4	1.7		0.0	0.0	0.0
6 Rings	0.0	0.9	1.1		0.0	0.0	0.0
Benzenes*	4.0	3.8	3.3		1.6	1.8	1.8
Napthalenes*	0.1	0.2	0.4		0.0	0.0	0.1

*Artifacts due to the fragmentation of certain cycloparaffins.

TABLE VII
¹H NMR ANALYSIS OF AROMATIC FRACTIONS

Sample Fraction	Tar Sands Bitumen			Big Horn Coal		Pitt Seam Coal	
	Mono-	Di- + Tri-	Poly-	Mono-	Di- + Tri-	Mono-	Di- + Tri-
Wt. % of Fraction in Sample	7.0	30.1	10.7	9.0	42.0	5.9	26.7
Monoaromatics, Mole %	100.0	53.7	49.1	100.0	16.4	100.0	15.6
Diaromatics, Mole %	0.0	46.3	50.9	0.0	69.7	0.0	63.5
Triaromatics, Mole %	0.0	<0.1	<0.1	0.0	13.8	0.0	21.0
Aromaticity, C _A	0.24	0.37	0.27	0.39	0.76	0.37	0.73
Average Molecular Weight*	339	284	404	204	169	218	181
Alkyl Substituents/Molecule	3.5	3.5	4.4	3.4	1.8	4.0	2.1
Carbons/Alkyl Substituents	5.3	3.7	4.9	2.7	1.7	2.6	1.8
Aromatic Rings/Molecule	1.0	1.5	1.5	1.0	2.0	1.0	2.1
Naphthene Rings/Molecule	1.4	0.9	1.5	1.3	0.3	1.5	0.4

*Does not account for O, N, S, etc.

TABLE VIII

¹H NMR ANALYSIS OF AROMATIC SHALE OIL FRACTIONS

Sample Fraction	Cut I			Cut II			Cut III		
	Mono-	Di-+Tri-	PNA	Mono-	Di-+Tri-	PNA	Mono-	Di-+Tri-	PNA
Wt. % of Fraction in Sample	8.3	4.2	2.3	8.0	13.4	5.6	5.3	9.3	1.3
Monoaromatics, Mole %	100.0	38.2	81.0	100.0	52.8	84.3	100.0	55.0	56.4
Diaromatics, Mole %	0.0	61.8	19.0	0.0	47.2	15.7	0.0	35.5	28.5
Triaromatics, Mole %	0.0	0.0	0.0	0.0	0.0	0.0	0.0	9.5	15.1
Aromaticity, CA	0.20	0.61	0.32	0.26	0.51	0.29	0.18	0.44	0.44
Average Molecular Weight*	413	183	283	316	204	311	448	248	248
Alkyl Subst./Molecule	4.4	3.3	4.6	4.0	3.6	5.2	5.4	3.9	5.5
Carbons/Alkyl Subst.	5.5	1.6	3.1	4.3	2.1	3.2	5.0	2.7	1.9
Aromatic Rings/ Molecule	1.0	1.6	1.2	1.0	1.5	1.2	1.0	1.5	1.6
Naphthene Rings/Molecule	2.5	0.4	1.1	1.5	0.5	1.2	2.2	0.7	0.3

*Does not account for N, O, S, etc.

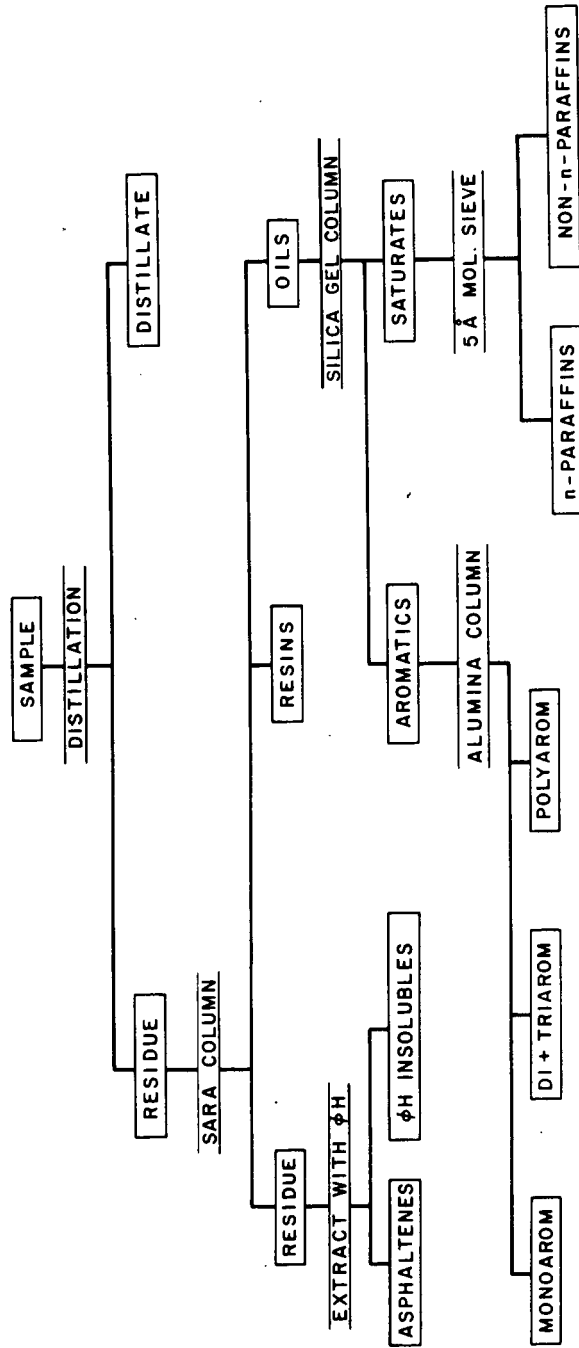


FIGURE 1.

Separation Scheme

FIGURE 2.
GLC of Saturates from
Tar Sands Bitumen

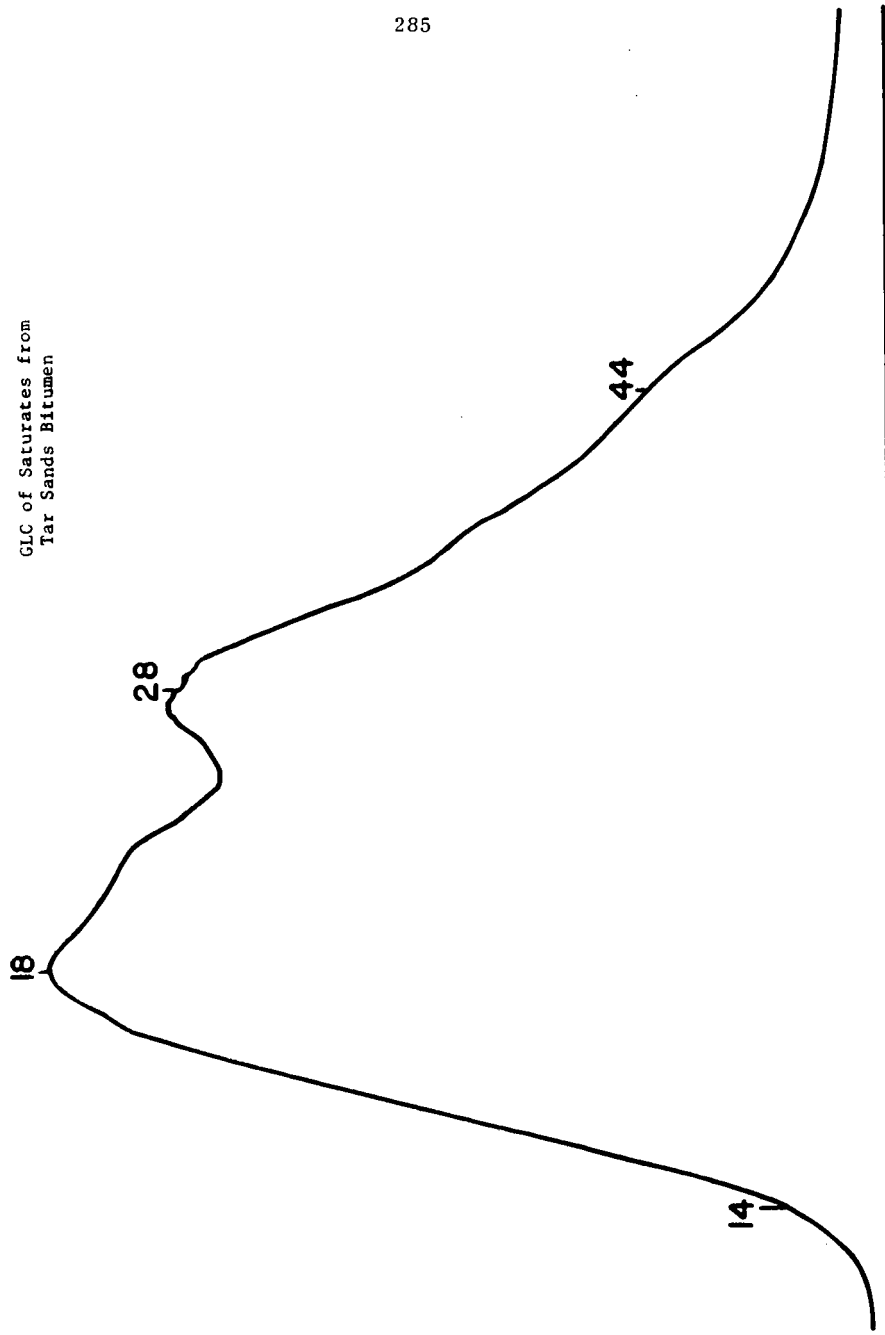
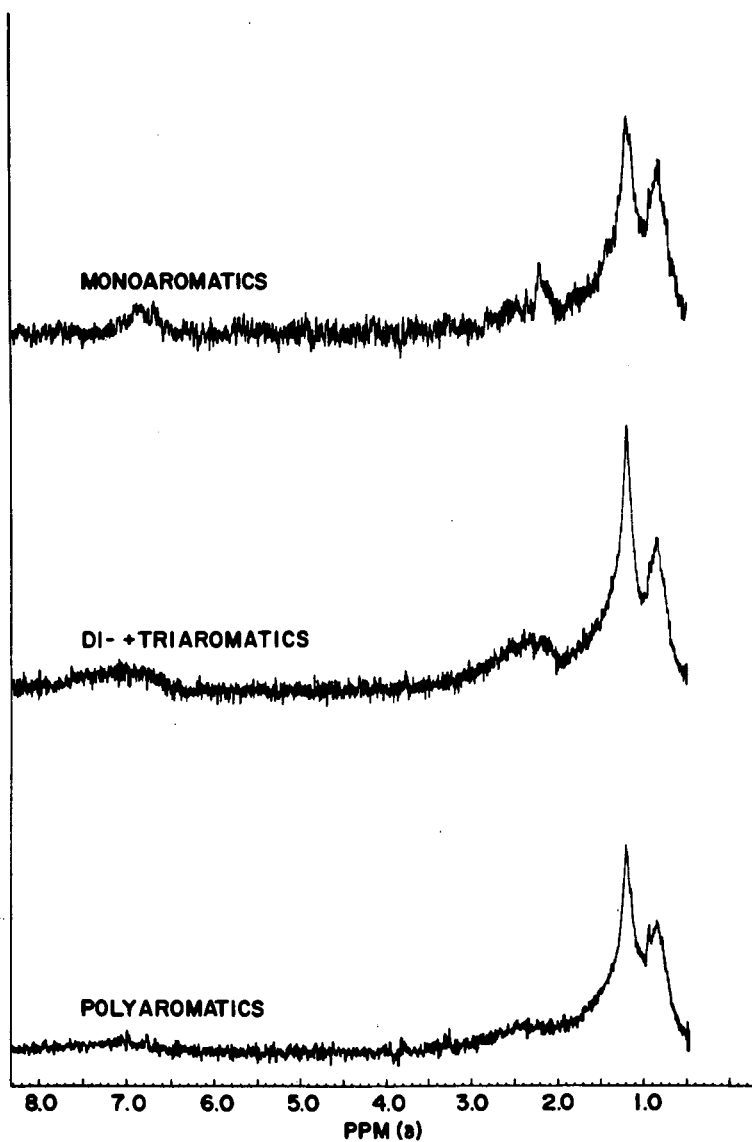


FIGURE 3.

**¹H NMR SPECTRA OF AROMATIC FRACTIONS
FROM TAR SANDS BITUMEN**



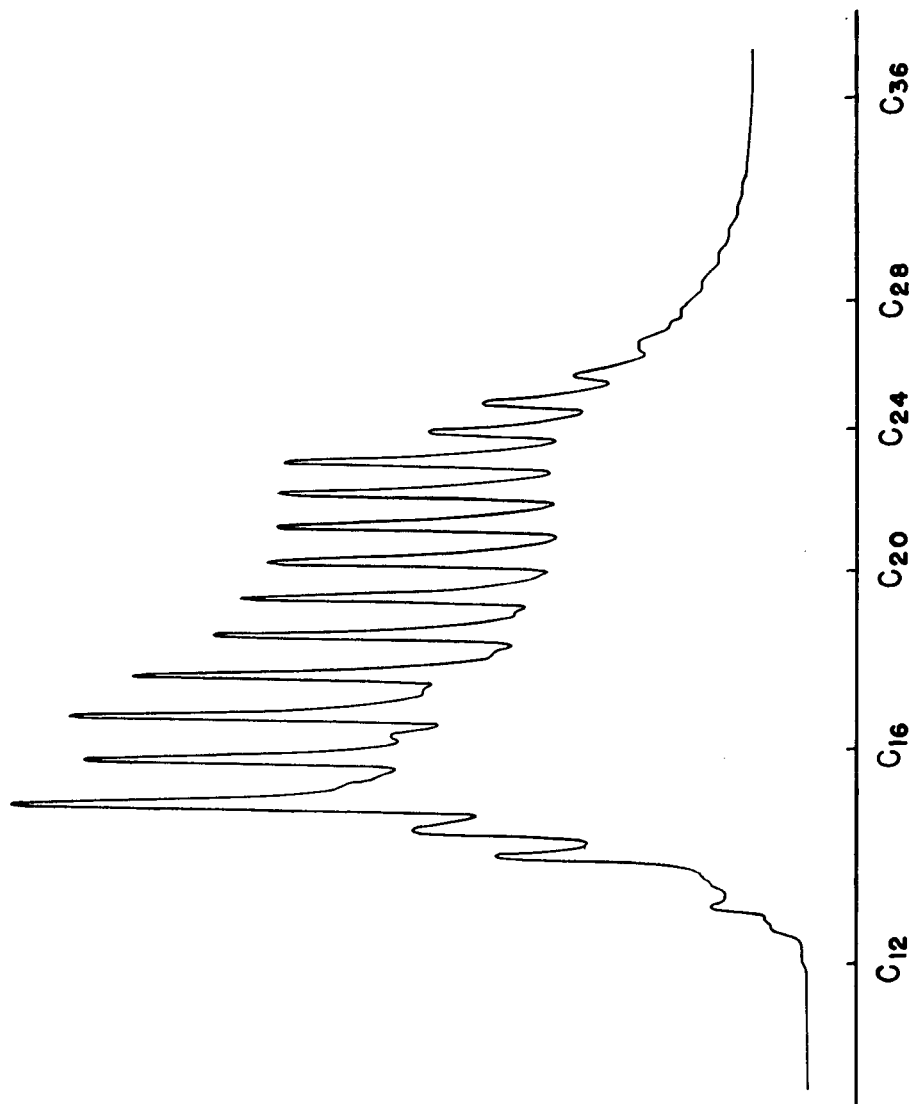


FIGURE 4.
GLC of Saturates from B18
Horn Coal Liquids

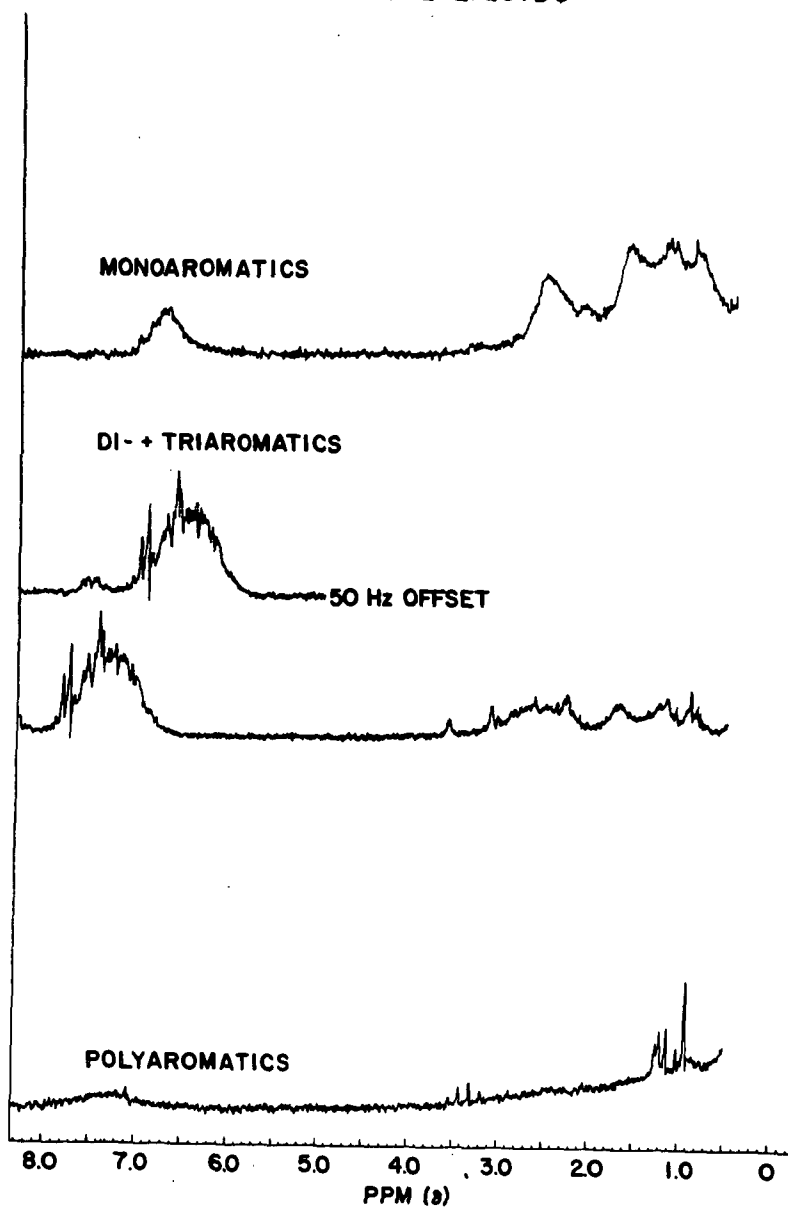
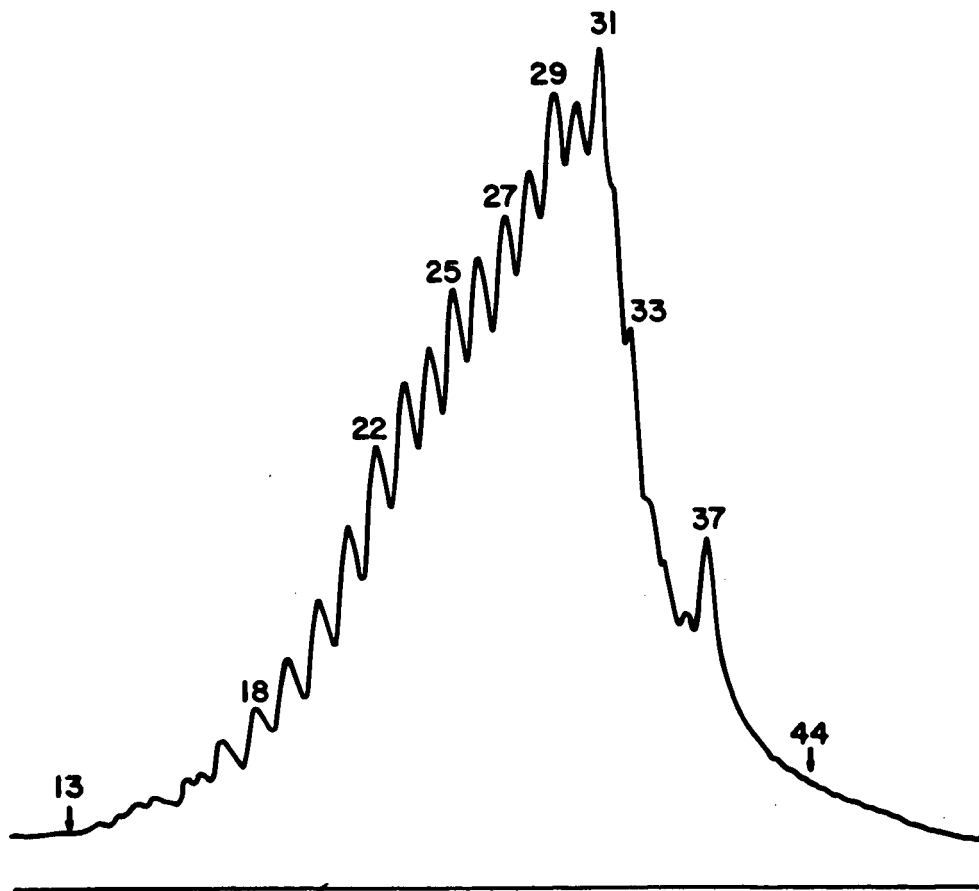
**¹H NMR SPECTRA OF AROMATIC FRACTIONS
FROM COAL LIQUIDS**

FIGURE 6.

GLC OF SATURATES FROM SHALE OILS



**¹H NMR SPECTRA OF AROMATIC FRACTIONS
FROM SHALE OILS**

